A substrate provided with a finish

The invention relates to a substrate provided at its visible side with a finish having a grain texture, with a suede type fine fibre upper side, in particular a grain leather with a polished grain side forming the upper side or a synthetic suede material with an upper side consisting of micro fibres, whereby the finish consists of a stabilised synthetic dispersion and is produced on a backing with a textured surface corresponding to the grain texture and a bonding layer formed of a stabilised synthetic dispersion containing polyurethane, which is applied to the upper side of the substrate. A nubuck type appearance of the visible side of the finish is also to be understood under the expression "grain texture".

Full grain leathers, so-called aniline leathers, which are merely coloured, but have no finish at their grain side, in desired manner show a particularly high air and watervapour permeability, but in these leathers the grain side is not wear resistant, scratch resistant, light fast and non-sensitive to contamination, so that these leathers cannot be used for the interior trim of vehicles and for the production of shoes.

It therefore already has been suggested to provide the upper side of a leather, and this being in particular a grain leather polished at its grain side, but also a split leather, as well as a synthetic suede material, with a finish showing a grain texture so that the visible side has the same required characteristics and has a leather type appearance.

In a known method the finish is initially produced separately on a backing of silicone rubber, in which the backing has a textured surface corresponding to the grain texture of the finish. In the production of this finish initially a

synthetic dispersion, which contains maximum 60% by weight but as a rule 40 % by weight solid portion, is applied by scraping, spraying, roller coating or casting onto the textured surface of the backing and allowed to stabilise by way of heat supply. Immediately after application the wet synthetic dispersion shows a smooth surface, however, on stabilisation this film produced by synthetic dispersion shrinks due to water withdrawal, whereby the dispersion sets into the valleys of the texture of the backing, and at the tips of the texture only a very thin or under circumstances even a non-continuous layer of the finish is created, in particular then if the finish has to show an attractive deep grain and consequently the backing has a correspondingly, strongly defined texture.

This disadvantage appears in particular also then if only a thin dispersion layer can be applied on the backing, in particular in the case of a strongly defined texture, because otherwise problems occur during drying, whereby in particular in the grain valleys of the textured backing it leads to bubble development and rupturing of the finish.

A further difficulty in the production of the finish on a textured backing consists therein that the aqueous synthetic dispersions containing as a rule the polyurethane required therefore with a solid portion of more than 50 % by weight are not obtainable in the market and on drying the low solid portions of the commercially usable dispersions cause a strong shrinkage.

If a finish, produced separately according to such a known method, is separated from the backing of silicone rubber, then the side facing the textured surface thereof forms the visible side of the finish, so that then the grain valleys of the finish only have a very small thickness, whereby by notching predetermined breaking points are created in the finish, which, in particular if the leather provided with such a finish is subjected to bending or tensions,

results in visible damage to the finish. This generally is the case if leather, provided with such a finish, is to be used for the manufacture of interiors of motor vehicles and of seat upholstery and also footwear material.

In order to avoid this disadvantage it hitherto has been necessary to provide at least one layer, as a rule several layers, between the finish and the surface of the leather for compensation. It accordingly has already been suggested to provide a thick compensation layer in order to compensate for the shrinkage loss of the dispersion initial application, which simultaneously serves as bonding layer.

Thus adhesion problems often occur between the individual layers so that at least a partial separation of the layers can take place.

A considerable disadvantage of the known leathers provided with a finish, in particular then if at least one compensation layer is provided, consists therein that the required air and water permeability is not present, because the compensation layer closes the pores or other open cells, which may be present in the thin finish. The breathing activity of the leather, provided with the finish, is thereby negatively influenced. In particular in case of a leather with a finish with a very coarse grain texture very thick compensation layers are to be provided for bonding with the leather, which influences the characteristics of the leather in unfavourable manner.

Thus, for example, it is known from US-A 4,923,732 to bond the finish to the leather surface by way of a thick compensation layer.

US –A 4,751,116 and the US-A 6,177,148 similarly show a leather in which the finish is bonded to the leather by way of several layers. One of the bonding layers thereby penetrates into the pores of the finish and fills these, whereby the water permeability is strongly reduced and an air permeability in practice is not present. For this reason it has been suggested to perforate the finished

leather mechanically. However, such mechanically produced perforations weaken the leather and lead to a contamination of the surface.

Also substrates are known, of which the finish is produced by the application of a polyurethane as well as a dispersion containing cross-linking agent produced on a warm backing. The application takes place according to the known method by scraping, casting or by means of rollers, whereby no uniform thick film type finish can be produced. Also on application by means of a known spraying method such thin films cannot be produced, because for achieving the grain texture hereby larger quantities have to be applied which leads to formation of films of different thickness in the grain tips and grain valleys.

The present invention has as object to avoid the mentioned disadvantages and to create a substrate of the type mentioned initially provided with a finish, which shows the required characteristics regarding its softness, friction resistance, in particular also the air and water permeability required for comfort, and of which the finish is produced of an aqueous synthetic dispersion free of solvents. Furthermore it is the object of the invention to avoid that artificial leather with a finish formed of polymer solutions and artificial leather with coagulated finishes always have to be applied by means of a scraper onto the textured backing, whereby the disadvantages of the different thicknesses particularly apply to these finishes. A finish consisting of coagulated polyurethane, if it comes into contact with a burning cigarette, is damaged on its surface in particular. Furthermore such finishes are not solvent resistant.

For solving this object the invention suggests that the finish has through-capillaries extending through its full thickness and essentially having the same thickness both in the region of the grain tips as well as in the region of the

grain valleys, and is bonded by way of a single thin bonding layer to the backing. Due to the arrangement of the through-capillaries both in the region of the grain tips as well as in the region of the grain valleys then, if merely a single thin bonding layer is provided, the required air and water permeability is considerably improved, whereby simultaneously it is ensured that the total finish has substantially the same thickness, has no weakened positions and at all positions has the same strength, so that also in the case of bending and tension of the substrate no damage to the finish takes place. A mechanical perforation of the substrate provided with the finish, for achieving the required air and water permeability which leads to a weakening of the substrate, therefore is not necessary in case of the embodiment of the substrate in accordance with the invention.

A further advantage consists therein that so-called "low water absorption leather" can be finished in the manner in accordance with the invention in which these leathers are breathing, therefore being air and water permeable, but in the case of a large water accumulation, as for example in the case of rain, the water, in contradistinction to the mechanically perforated leathers, cannot pass through the leather.

The capillaries suitably have different cross-sections with a diameter between 0,005 mm and 0,05 mm, preferably between 0,009 mm and 0,02 mm, whereby optimum conditions result if at least 100 capillaries, preferably at least 250 capillaries are provided on a surface of 100 cm^2, and these extend substantially in straight line.

According to a preferred embodiment of the invention the capillaries are distributed irregularly in the finish, so that the visible side of the finish has the appearance of the pore texture of a natural skin.

An optimum air and water permeability is guaranteed then if, according to a further characteristic of the invention, the bonding layer has interruptions or weakened spots of reduced thickness. Thereby it is ensured that air and water vapour can pass practically unhindered through the through-pores, which are formed by the capillaries in the finish and by the interruptions communicating with the capillaries in the bonding layer, and thus, for example, when using the substrate for footwear the occurring foot sweat is taken up by the wearer himself and is led off by way of the bonding layer and the finish. When using the substrate in accordance with the invention for upholstered furniture the occurring moisture is transported by the finish and the bonding layer to the substrate and is absorbed by this. Even in the case of hydrophobized leathers with a thickness of more than 2 mm in the embodiment in accordance with the invention a water permeability of more than 1,5 mg/cm^2 per hour according to DIN 53333 is achieved.

The mentioned through-pores also can be made visible in that a coloured contrast agent is applied to the surface of the finish and is allowed to draw into the pores, and after drying sectional photographs are made of the substrate provided with the finish.

The interruptions or weakened spots in the bonding layer are achieved preferably thereby that the bonding layer is merely arranged partially on the surface of the substrate, so that no continuous layer is formed. It has been shown that also in this case a sufficient bonding between the substrate and the finish is given, whereby a very high air and water permeability is ensured. Furthermore the required softness and an extremely high frictional resistance is achieved so that the required parameters are fulfilled, in particular for interiors in the motor vehicle industry, whereby nevertheless a good adherence between the finish and substrate is ensured.

According to a preferred embodiment of the invention the bonding layer has a punctiform, screen or grid type, in other words net-like texture, so that interruptions are present and no full surface, bending stiff sandwich construction exists, which negatively influences the air and water permeability and also the bendability. In particular cases it is sufficient for improving the mentioned characteristics, if the bonding layer has a maximum thickness between 0,01 mm and 0,05 mm and at its weakened spots a thickness between 0,002 mm and 0,01 mm, in which case a good air and water permeability is achieved by way of these thin weakened spots and by means of which also the bendability and the surface adhesion of the leather is considerably improved.

If the upper side of the substrate is fibrous, in particular formed to be fine fibrous, then it is advantageous if the bonding layer is arranged predominantly in the region of the fibre peaks so that hollow spaces which cause a pump effect are kept free between these fibre peaks, when loading the substrate provided with such finish. It has been shown that in this case a sufficient bonding between the fibrous surface of the substrate and the finish is achieved whereby the required high air and water permeability, in particular also due to the mentioned pump effect, is ensured. This pump effect causes that, when applying a pressure on the finish, for example by seating on a seat provided with a finish substrate, the finish is pressed together, and on pressure relief of the finish a suction effect is created whereby moisture is rapidly absorbed by the substrate. When using leathers with upper surface errors as substrates the advantage also exists that these are not any longer visible in the case of finished leather because the upper side of the substrate is polished for achieving a high air and water vapour permeability in combination with the pump effect.

It is suitable if the bonding layer consists of a stabilised, polyurethane containing cross-linked synthetic material dispersion, in particular of a

stabilised polyester-polyurethane-dispersion. Thus it is advantageous if the polyurethane containing dispersion has at least a crystalline or a partial crystalline structure. After its stabilisation but before its cross-linking, the bonding layer, consisting of such a dispersion, is thermoplastic and has a very low softening point, in particular if it contains still between 2% and 10 % water but has a touch of being dry. Such a bonding layer ensures, on the one hand, a good bonding between the substrate upper side and the finish, but also ensures that it does not penetrate deeply into the intermediate spaces between the fibres or fibre tufts at the substrate upper side and hardens these, and if it is cross-linked, is heat resistant.

It is advantageous for a good bonding if the synthetic dispersion contains additives acting adheringly, in particular soft resins or soft polymers, in particular acrylate, by means of which the adhesion effect of a dispersion, already partially stabilised, is improved.

According to a further characteristic of the invention the synthetic dispersion can contain micro hollow spheres with a diameter of less than 21 µm, which form small drops interiorly containing a gas, at the upper side of the substrate and thereby prevent further penetration of the applied synthetic dispersion into the substrate.

It has been found to be favourable if the bonding layer has a weight per unit area of between 20 g/m^2 and 90 g/m^2. In the case of substrates with a non-polished or only finely polished upper side the weight per unit area amounts suitably between 20 g/m^2 and 45 g/m^2, in the case of substrates with deeply polished upper side and in the case of split leathers suitably between 45 g/m^2 and 90 g/m^2.

Optimum qualities regarding air and the water vapour permeability are achieved then if the finish has not only substantially the same thickness but also approximately the same texture and the same density in all cross-sectional regions and therewith has at all positions the same strength and no weakened positions are present, which lead to damage of the finish on bending and tensions of the substrate provided with the finish.

The finish consists preferably of a combination of a stabilised polyurethane dispersion containing a cross-linking agent with a high softening point and a stabilised polyurethane dispersion containing a cross-linking agent with preferably crystalline or partial crystalline structure with a low weakening point, which dispersion is thermoplastic prior to the cross-linking. The required characteristics can be achieved in optimum manner by means of the combined use of a polyurethane dispersion, which, prior to cross-linking, already leads to a temperature resistant film with elastomeric characteristics, with a thermoplastic polyurethane dispersion with preferably crystalline or partial crystalline structure, as used as raw material for adhesives.

According to a further characteristic of the invention the finish can contain micro hollow spheres with a diameter of less than 21 µm forming closed cells.

The finish shows, in contradistinction to known finishes, no foam texture, which stores liquid in undesired manner, but is air and water vapour permeable by means of the through-capillaries.

According to a further characteristic of the invention the grain tips of the finish can have microscropical small smooth raised parts in order to avoid or reduce contamination of the finish, in particular in case of light colours. However, the invention also allows providing a nubuck texture to the visible side of the finish out of which fine hairs protrude, which also form raised parts. The raised parts

suitably have a diameter between 3 µm and 60 µm, preferably between 5 µm and 15 µm, as well as a maximum length of 110 µm and are tightly arranged. These raised parts, which can have the appearance of fine hair, cause that wet contamination of the smooth surface of these raised parts remain and do not sink down into the micro intermediate spaces between the grain tips or into the nubuck texture, and therewith prevent dirt from adhering over the total surface at the upper side of the finish.

The positive effect is furthermore improved if the finish contains waxes and/or silicones at its visible side by means of which the surface tension of the finish is changed relative to water.

Furthermore, in accordance with the invention, the visible side of the finish can be provided with a very thin finish, which does not negatively influence the air and water vapour permeability, by way of which the grip as well as the gloss degree of shine can be influenced.

A polymer impregnation, which possibly may be present and which is drawn into leather used as substrate and serves for binding buffing dust and grain stabilisation, has no influence on the air and water vapour permeability and is left out of consideration.

In accordance with the invention a strong synthetic woven or knitted fabric with protruding fibres, which preferably has a weight per unit area of more than 250 g/m^2 is provided on the side of the substrate opposite to the upper side, in particular the fresh side in order to provide more volume to the finished substrate and to create its visible side more gripping friendly. The adhesive bonding between this woven or knitted fabric and the substrate takes place thereby that only between the fibres an adhesive effect is produced. This woven or knitted fabric can be covered by way of a thin coating.

Animal hides from which leather is produced, are expensive, so that these hides have to be used optimally. If the formation of the finish on the overall leather produced by way of such animal hide takes place in a single working step, then during the further use, due to the different characteristics in the individual regions of the hide a considerable quantity of waste results. In order to avoid this waste insofar as possible, and to ensure an optimum utilisation of the leather hide, it is of advantage, in accordance with the invention, if shaped sections are separated out of this hide, whereby in the case of a shaped section in the flank or belly region the finish shows a strongly defined grain texture and in the core region a flat grain texture.

The method in accordance with the invention for producing a finish showing a grain texture at the visible side of a substrate, in particular a grain leather, a split leather with polished upper side or a synthetic suede material with an upper side consisting of micro fibres, whereby initially for forming the finish an aqueous synthetic dispersion of a backing consisting of silicone rubber, which has a surface texture according to the grain texture of the finish, applied and allowed to stabilise into a film, furthermore in the upper side of the substrate a synthetic dispersion forming a bonding layer is applied, and furthermore the substrate with this upper side placed onto the film and subjected to a pressure and heat treatment, consists essentially therein that the synthetic dispersion containing solvent free polyurethane as well as a cross-linking agent is applied on a backing having a uniform temperature of less than 105°C, that this synthetic dispersion on touching on the backing is stabilised immediately and, after water evaporation, a uniformly thick film having a texture with thickness of less than 0,04 mm is formed. In this manner a thin finish is produced on the backing, which is overall of similar thickness and has capillaries distributed over its total thickness.

The synthetic dispersion consists of a combination of a polyurethane dispersion containing a cross-linking agent with a high softening point, and a polyurethane dispersion containing a cross-linking agent with preferably crystalline or partially crystalline structure with a low softening point, which dispersion is thermoplastic prior to the cross-linking.

The application of the synthetic dispersion onto the backing takes place by means of a fine spraying fog produced by way of spraying nozzles having a very small diameter in such low quantities that water is withdrawn from the synthetic dispersion already on the way to the heated backing and in any case this synthetic dispersion immediately on touching onto the backing is stabilised such that the synthetic dispersion cannot sink down into the grain valleys of the textured backing, but in any case at all positions forms a uniformly thick netting type film, whereby the mentioned capillaries are created.

The textured surface of the backing preferably is produced by taking a cast from the grain texture of a natural leather.

In particular then if the surface of the finish has to show a suede effect, it is also possible to produce the textured surface of the backing by way of laser treatment, so that a texture with finest hairs is created on the surface of the backing. The textured surface of the finish produced by the laser treatment can be multiplied by way of a master.

Preferably a backing consisting of additionally cross-linked silicone rubber with a shore hardness between 25 Shore A and 70 Shore A can be used. Such a backing is pressure elastic in desired manner so that during the following pressure and heat treatment the grain appearance is not destroyed. Furthermore, during the laser treatment of additionally cross-linked silicone rubber no free radicals hindering the forming are created so that depressions

are formed in the silicone rubber recesses can be formed which later on have the appearance of finest hairs or finest fibre tuffs on the finish and lead to a nubuck effect.

Suitably the backing consists of a heat conducting silicone rubber with a density of more than 110 g/cm^2, preferably of more than 120 g/cm^2, and therewith has a good heat conductivity, which is necessary for uniform heating during the spray application of the synthetic dispersion. For increasing the heat conductivity inorganic fillers can be embedded in the backing. Preferably the backing has a thickness of between 1 mm and 3 mm and is bonded to a heat conductive, preferably a support consisting of aluminium, which has a thickness of between 1 mm and 3 mm. This heat conducting support ensures a uniform heat distribution onto the backing.

The bonding of the backing to the heat conducting support takes place in accordance with the invention by means of a single component adhesive, into which a thin suede material of synthetic fibres with a weight per unit area of less than 150 g/cm^2 can be embedded. By means of this embedding the heat conductivity is not hindered, but the heat expansion of the silicone rubber is strongly restricted.

A synthetic dispersion is applied to the upper side of the substrate, which consists essentially of a polyurethane dispersion with a low softening point and preferably crystalline or partial crystalline structure and a cross-linking agent, for forming the bonding sheet in accordance with the invention and this being such that it stabilises rapidly on touching the upper side of the substrate and that a non-continuous bonding layer is created. However, such a synthetic dispersion can also be applied so that a bonding layer with weakened spots of reduced thickness is created. The application thereby takes place similar to the application of the synthetic dispersion on the backing of silicone rubber for

forming the finish, but in the present case because the dispersion on touching the upper side of the substrate water is withdrawn due to the water absorption by the substrate, so that on the upper side similarly a net like film is formed as is the case when the dispersion for forming the finish touches on the warm backing.

If the leather used as substrate is hydrophobized and thereby is in a position to take up less water, then it is suitable to heat the leather before applying the dispersion forming the bonding layer.

Compositions, such as known for the production of adhesives, can be used for the dispersion forming the bonding layer.

The synthetic dispersion applied on the upper side of the substrate should be gripping dry, but preferably still contain residue moisture, prior to the upper side of the finish being provided with this synthetic dispersion, is placed onto the film arranged on the backing, which is substantially water-free and shows the netting texture, and the cross-linking may not have taken place yet.

Thereafter, in accordance with the invention, the film forming the finish and being on the backing and showing a netting texture with the backing placed thereon forming the bonding layer with the synthetic dispersion, is pressed between pressure elastic plates at a temperature between 60°C and 105°C and a pressure of maximum 5 kg/cm^2. During this pressing, which takes place under heating effect, the film forming the bonding layer and being on the substrate, becomes softer because its softening point is lower than that of the film forming the finish and being on the backing, so that the capillaries in the finish are retained. The film forming the bonding layer becomes sticky but not liquefied so that the capillaries in the finish are not closed by it and this film does not flow together, thus retains it texture and the interruptions in the

bonding layer are retained. It therewith is ensured that, on the one hand, a sufficient bonding between the finish and the upper side of the substrate takes place, on the other hand the required air and water permeability is ensured.

The substrate provided with the finish, after pressing finally can be subjected in suspended position to a residue drying for the purpose of complete drying and cross-linking.

The invention is explained in more detail by means of the drawings. Figure 1 shows in section a known method for producing a finish on a backing consisting of a silicone rubber and Figure 2, in section, the construction of a leather provided with a finish produced according to the known method. Figure 3 shows in section a leather provided with a finish in accordance with the invention and Figure 4, in a substantially enlarged representation a section through a leather provided with a finish in accordance with the invention. Figure 5 shows in substantially enlarged cross-section a grain tip of the finish. Figure 6 represents in section a further embodiment of a leather provided with a finish in accordance with the invention. Figure 7 shows in a substantially enlarged sectional representation a further embodiment of a leather provided with a finish in accordance with the invention, and Figure 8, similarly in section, a leather provided with a finish in accordance with the invention, which on its neat side is provided with a synthetic woven or knitted fabric. Figure 9 represents schematically an apparatus for producing the finish on a backing and Figure 10 schematically an apparatus for bonding the finish to the upper side of the leather. Figure 11 shows photographically the visible side of the finish provided on leather in accordance with the invention.

As is clear from Figure 1 the known production of a finish 1 on a backing 2 consisting of silicone rubber took place thereby that a synthetic dispersion is applied by scraping, spraying, roller application or casting the surface 3 of this

backing 2 textured corresponding to the grain texture of the finish to be produced, which dispersion contains about 55 % solid portion in the example of the embodiment according to Figure 1. Following directly on the application this synthetic dispersion shows a flat upper side 4 represented in dotted lines in Figure 1. After drying by heat supply across the backing 2 the synthetic dispersion shrinks due to water withdrawal, so that the film formed thereby has a surface 5 showing grain valleys and grain tips. As can be seen from the drawing, the resulting film in the region of the grain tips 6 projecting from the backing 2 is very thin so that there the danger of ruptures and damage exists, because the synthetic dispersion sinks down into the intermediate spaces between the grain tips 6 projecting from the backing 2.

Figure 2 represents a known leather 7, which is provided with a finish 1 according to Figure 1. The side of the finish 1 facing the backing 2 in Figure 1 now represents the visible side so that, as is clear from the drawing, the grain valleys 8 of the finish 1 have an extremely small thickness. Several compensation layers 9 and 10 must be provided between the leather and the finish 1 in order to compensate this disadvantage, whereby the compensation layer 9 in the example shown in the drawing consists of a foam material and the compensation layer 10 forms the adhesive layer. These relatively thick compensation layers increase the overall thickness in undesired manner and cause in particular that the pores or the like possibly present in the finish 1 are closed so that air permeability exists no longer and the water permeability is reduced considerably.

In the Figures 3 and 4 a leather 7, provided with the finish 1 in accordance with the invention, is shown, in particular a leather or a split leather polished at its grain side. As is clear from the drawing the finish 1 here shows substantially the same thickness d in the region of the grain tips and in the region of the grain

valleys. Thus no weakened positions of reduced thickness are present, which undesirably influence the stability of the finish 1.

As is further clear from the Figures 3 and 4, the finish 1 shows through-capillaries extending over the total thickness of different cross-sections substantially linearly by way of which the required air and water permeability is ensured. These capillaries are irregularly closely arranged next to each other so that the finish 1 has the appearance of the pores of an animal hide and has a cross-section between 0,009 mm and 0,02 mm.

The bonding of the finish 1 to the leather 7 takes place by means of a single very thin bonding layer 12, which is substantially air and water permeable.

For this purpose the bonding layer 12 can be provided merely partially on the surface of the leather 7 or can have weakened spots of reduced thickness and/or interruptions.

The finish 1 consists of a stabilized dispersion, which contains a portion of polyurethane with at least partially crystalline structure as well as a cross-linking agent, and has substantially the same texture and the same thickness in all cross-sectional regions.

As can be seen from the right hand part of Figure 5, in which a grain tip of the surface of the finish 1, having a grain texture, is shown in a considerable enlarged scale, the grain tips of the finish 1 can be provided with microscopical small closely arranged smooth raised parts 13 with a diameter of between 5 µm and 15 µm, which can have the form of fine hair or finest fibre tufts and show a maximum length of 110 µm. These raised parts cause that particularly wet contaminations remain on the smooth surface and do not drop down into the hollow spaces between the grain tips. Thereby the known lotus effect is

utilised to some extent and it is avoided that dirt is fixed completely on the surface.

The same object is served if the region of the finish neighbouring on the backing 2 of silicone rubber, which then forms the visible side, contains small quantities of substances, such as waxes or silicones, which change the surface tension of the finish relative to water.

Figure 6 shows, in enlarged cross-section, an embodiment in which the leather has a suede type upper side 14, which is formed when using a grain leather from the polished grain side and on use of a split leather from the finally polished finish side. Fibres or fibre tufts 15 project from this upper side 14, between which hollow spaces 16 are kept free. The upper side 14 is provided with a porous finish 1, which is applied on a backing showing a textured surface consisting of silicone rubber and by heating thereof the same stabilised synthetic dispersion is formed. The finish 1 shows through-capillaries, which are not represented in the drawing. The pore texture formed by these capillaries can be established easily if the finish is released from the leather 7 mechanically or by means of chemical agents and then held under slight stretch against a light source.

The bonding of the finish 1 to the upper side 14 of the leather takes place by way of a bonding layer 12, which is arranged, as the drawing shows, merely partially and this being in particular in the region of the tips of the fibres or fibre tufts 15 so that the hollow spaces 16 between these fibres or fibre tufts 15 are held substantially uncovered. Thus a high air and water permeability is created, which is further improved thereby that a pumping effect is created when applying pressure to the leather 7 provided with a finish 5.

As the drawing clearly shows in the strongly enlarged section of the object of the invention, the bonding layer 12 is located substantially on the suede type upper side 14, which has the characteristic appearance of a polished split suede leather, which has a so-called "chalking effect" before application of the finish 1. The bonding layer 12 concentrates on the upper region and partially on the side region of the fibres or fibre tufts 15, whereby merely a reduced portion of the bonding layer 12 is arranged in all cases at the base of the hollow spaces 16 between these fibres or fibre tufts 15, which has no relation with the bonding layer 12 present in the upper and side region of the fibres or fibre tufts 15 so that inbetween air chambers are created.

Figure 7 shows an embodiment in which a grain leather 7 polished at its grain side or a split leather 7 with polished upper side is provided with a finish 1, which shows through-capillaries 11 extending through the total thickness. The finish 1 consists of a stabilised cross-linked synthetic dispersion containing polyurethane and is produced separately thereby that a silicone rubber provided with a textured surface, an aqueous polyurethane dispersion is applied in the form of a fine spraying fog onto a warm backing 2, which fog stabilises immediately after touching the backing, whereby the required through-capillaries 11 are formed in the stabilised dispersion.

The finish 1 produced thus separately is bonded, directly after its stabilisation, by way of a bonding layer 12, applied on the upper side of leather 7, to this upper side. In the embodiment shown in Figure 7 this bonding layer 12 shows a punctiform, screen or grid type, therewith a net type texture, so that only at individual positions or points a bonding between the upper side of the leather 7 and the finish 1 is produced and inbetween interruptions 17 are created, which communicate with the capillaries 11 in the finish 1 and thereby ensure the required air and water vapour permeability.

The interruptions 17, which form a net type texture, can have any desired form, and, for example, be shaped round, rectangular or linear, but also can have any other suitable form.

Not only such interruptions 17 are provided in the bonding layer 12 in the embodiment shown in Figure 8 but this also has weakened positions 18, of which the thickness is considerably less than the remaining thickness of the bonding layer 12, so that by means of these weakened positions 18 the air and water permeability is considerably increased and the bendability and the adhesion between the upper side of the leather and the finish is improved.

The bonding layer 17 hereby suitably has a maximum thickness between 0,01 mm and 0,05 mm, whereby the weakened positions 18 merely have a thickness between 0,002 mm and 0,01 mm.

The fresh side 19 of the leather 17 in the embodiment shown in Figure 8 is provided with a strongly grid like synthetic woven or knitted texture 21 with projecting fibres, which can be covered by way of a thin coating 20. Thereby more volume is provided to the finished leather.

The bonding between the fresh side and the woven or knitted fabric takes place by means of an adhesive, such that an adhering effect is produced only between the fibres.

Such an embodiment is of advantage in particular in shaped sections formed from the leather in accordance with the invention for producing footwear because in this case the open pore thin coating serves as lining material and a separate application of such a filling material is therewith not necessary. As a result of the large water permeability of the leather in shoes a discharge of the foot sweat, which occurs, and due to the large air permeability an aeration of

the shoe inner space, when using the leather in accordance with the invention for automobile seats and upholstered furniture, takes place.

The through-capillaries 11, provided in the finish 1, which form a netting texture, on illumination are already clearly visible at a 45 times enlargement and a stretch of about 25 %. In a mechanical or chemical removal of the finish from the bonding layer 12 using the aid of solvents, it already can be seen at 16 times enlargement that the bonding layer 12 has both thick positions as well as weakened positions and that in the weakened positions also porous formed interruptions are provided. The finish film has a maximum thickness of 0,06 mm at a pressing pressure of 2 kg/cm^2 for establishing the thickness of the loosened finish.

In all described embodiments both in the finish 1 as well as in the bonding layer 12 micro hollow spheres with a diameter of less than 21 µm can be provided.

The leather in accordance with the invention, has, relative to the air and water permeability, similar up to the same characteristics as semi-aniline leather and is superior to a leather provided mechanically with perforations, but its visible side is also mechanically well loadable as well as light fast and dirt rejecting.

The present invention is applicable in particular to cowhide leather, but also to pig, calf, goat and sheep leather polished on its grain side, in particular then if such leather is also used for footwear production, furthermore also in the use of synthetic velvet leather as substrate.

The production of the finish 1 is explained by way of Figure 9 in more detail. A pressure elastic backing 2, of which its textured surface 3 corresponds to the grain texture of the finish to be produced, is joined fixedly to a heat conducting

support plate 23 of aluminium sheet, is heated by way of heating arrangements such that the surface 3 of the backing 2 has a temperature of about 80°C. Onto this heated surface 3 a polyurethane dispersion in the form of a fine spray fog 25 is applied by way of spraying nozzles 24 having a small diameter while the backing 2 moves in the direction of the arrow 26. At the latest on contacting the warm surface 3 of the backing 2 a stabilisation of the spray fog 24 by water withdrawal takes place so that a thin net type film having capillaries 11 is formed on the backing 2. As soon as this film is grip dry, a leather 7, on the upper side of which a synthetic dispersion forming the bonding layer 12 has been applied, is placed with this upper side onto the film and is pressed together with the backing 2 in a press shown in Figure 10. This includes two metallic pressing plates 27, 28, in which heating elements 29 are embedded. The pressing plates 27, 28 are hydraulically movably supported on supports 30.

The upper pressing plate 27 is provided with a pressure elastic layer 31. The leather 7, which has been placed with the upper side showing the bonding layer 12 onto the finish 1 situated on the backing 2, is thereupon positioned together with the backing 2 between the pressing plates 27, 28, whereupon, by means of these pressing plates, a controllable pressure of about 3,5 kg/cm^2 is applied and simultaneously the pressing plates 27, 28 are heated to a controllable temperature of about 90°C. Due to the pressure elastic support 31, on the one hand, and the pressure elastic formation of the backing 2, on the other hand, it is ensured that during a pressure application the capillaries 11 in the finish 1 and the interruptions in the bonding layer 12 are retained and therewith the required air and water permeability is ensured.

Figure 11 shows the photograph of a finish produced on a backing 2, as the leather in accordance with the invention has. The right hand section A was illuminated by means of an illumination source when taking the photograph

and clearly shows that the finish has a net type texture, that is through-capillaries, the left region B, in which the underside was covered, clearly shows the grain texture of the finish.

By means of the drawings the invention was explained relative to a leather as substrate. In place of the leather also a synthetic velvet material can be used as substrate.

Example 1:

A grey chromium-tanned calf leather, which is low in fogging with a thickness of about 1,2 mm and a size of 2,10 m^2, is slightly polished on its grain side by means of sand paper grain 280, and this being such that the hair pores are substantially retained. The leather is walked thereafter for six hours.

A polyurethane dispersion mixture is applied in a quantity of 88 g/m^2 on a pressure elastic backing of silicone rubber with a thickness of about 2 mm, which is bonded by glueing at its underside to a support plate of aluminium sheet of thickness 1,5 mm and which has a textured surface, which in negative corresponds to a natural full grain calf leather skin, and has a temperature of 91°C all over. The dispersion mixture consists essentially of 680 g of a thermoplastic polyurethane dispersion with a softening point of about 195°C, which, after water withdrawal, cannot be brought to melting, because the destruction temperature is below the melting temperature, and of 250 g of a fine particle thermoplastic polyurethane dispersion with a softening point of about 62°C, of which the melting point is at about 95°C and of which its adhesive point starts at a temperature of about 55°C directly after drying but before the cross-linking.

Furthermore this dispersion mixture has 4 % by weight of a 80 % polyisocyanate cross-linking agent, relative to the polyurethane solid material portion of the dispersion, 8,5 % by weight black pigment relative to the polymeric solid material portion, 2,5 % by weight of a silicone handle modifier with a solid portion of about 45 %, 1 % by weight micro hollow spheres relative to the overall weight with a diameter smaller than 21 µm, as well as 0,5 % by weight of a thickener on acrylate basis. This mixture has a polymer solid material portion of about 35 % by weight. The application takes place without air admixture at a pressure of 65 bar by way of two spray nozzles, which each have a diameter of respectively 0,46 mm.

The two spraying nozzles are arranged relatively spaced apart in series at a spacing of 80 cm from the continuous backing in movement direction thereof and move transversely to this movement direction. The backing is somewhat larger than the calves leather. After about 14 seconds the backing has passed the spray station with the two spray nozzles and still has a temperature of about 59°C. After being subjected to a two minute application with dry, warm air, of about 85°C the finish, consisting of a net type film, is free of water or almost free of water.

At the same time a dispersion containing a polyurethane mixture is sprayed onto the leather, also without air admixture, by means of two spraying nozzles, which have a nozzle diameter of 0,52 mm, at a spraying angle of about 80° emerging out of the nozzles. The application quantity amounts to about 90 g/m^2 moist. With this spray application quantity so much water is withdrawn by the wicking effect after reaching the leather that here also a net type texture with many continuous capillaries is created. Also without heat supply the spray coating is gripping dry after three minutes and forms a thermal plastic bonding layer, and the leather can be placed together therewith onto the finish, which is

still located on the preferably still warm backing and be bonded to this finish between pressure elastic supports in a heated press.

The heat is rapidly absorbed by the press and passed on to the thermoplastic bonding layer due to the good heat conductivity of the support plate consisting of aluminium. A delay time in the press of less than 25 seconds is sufficient at a pressure heating plate temperature of 90°C, a pressure of about 2 bar at the leather and an entry temperature of the backing with the superimposed leather of 48°C. The bond between the pressure elastic surface of the backing and the support of aluminium does not only provide advantages during pressing but also during spraying because the warm aluminium plate serves as heat sink and continuously emits heat to the backing during the spraying procedure.

The thermoplastic polyurethane dispersion mixture, forming the bonding layer, consists basically of 700 g a fine polyurethane dispersion with a softening point of about 62°C and a starting adhesive point of about 55°C, 180 g very soft polyacrylate, 200 g polyurethane with a softening point of about 170°C, 9 % by weight cross-linking agent relative to the overall composition, as well as 3 % by weight black pigment. The completed leather has, after polishing, almost the same softness as before. It has a water vapour permeability of 3,6 mg/cm^2.h and is so strongly air permeable that air can be blown through by the mouth.

Example 2:

A chromium-free tanned fogging poor black cowhide with a thickness between 1,10 mm and 1,25 mm and a size of 5,2 m^2 was polished by means of buffing paper grain 150 on its grain side and subsequently was milled (walked) for 12 hours. After the milling the flanks are spongy and double skinned and during polishing of the overall hide by means of known methods lead thereto that

after polishing about 50 % of the area during treatment of the surface became non-usable with a medium fine texture.

The core piece of the hide measured 1,95 m^2, which, after the milling, still was somewhat grain-fixed and suitable for polishing by means of a medium fine impregnation. This part was removed from the hide and prepared.

Thereby on a 90°C heated support, of which the textured surface corresponded in negative to medium fine nappa texture, a synthetic dispersion mixture in a quantity of 135 g/m^2 was applied by means of three spraying nozzles as described in example 1, so that a net type film forming the finish was created. The composition of the dispersion mixture differs from that given in example 1 merely therein that in place of 680 g non-thermoplastic polyurethane only 580 g and in the place of 250 g thermoplastic polyurethane 350 g was used.

During the overall spraying procedure the surface of the backing is warm because the support plate of aluminium sheet transmits heat to the backing.

About simultaneously the leather core piece, which, as described in example 1, onto which the synthetic dispersion is sprayed for forming the bonding layer, is placed onto the somewhat 39°C warm backing as described in example 1 and is pressed together. After the pressing procedure the leather was stored suspended for 30 minutes and then placed onto a palette. The prepared surface shows no funnel type collapsing positions, the numerous through-capillaries, which are present, are not visible. The water vapour permeability amounts to 2,9 $mg/cm^2.h$. Air can be blown through the leather by means of the mouth.

Example 3:

Coarse shaped sections for vehicle seats are punched out of spongy leather flanks. The same mixture is sprayed in the same quantity as described in example 1 in a first step by means of two spraying nozzles onto a 95°C warm pressure elastic backing of silicone rubber, of which the textured surface in negative corresponds to a very coarse grain and in which the differences between grain tips and grain valleys on the average amount to 0,05 mm. Thereby both on the grain tips as well as in the grain valleys a uniformly thick, netting type film forming the finish is created. Thereafter, a mixture, as described in Figure 2, is sprayed in a quantity of 60 g/m^2 by means of a spray nozzle onto the approximately 65°C warm film located on the backing. On reaching the first warm spray application this spray application also is stabilized and therewith strengthens the first film uniformly both in the region of the grain tips and also in the region of the grain valleys. By means of a uniformly running application roller a thermoplastic dispersion mixture according to example 1 in a quantity of about 55 g/m^2 forming the bonding layer is applied thus onto the leather that a predominantly continuous film with thicker and thinner zones is created. The placing and pressing together takes place as described in example 1.

The finished leather is no longer spongy, is soft and has a water vapour permeability of 1,9 mg/cm^2 .h, and air can be blown through.

Example 4:

A finely polished cowhide leather with a thickness between 1,2 mm and 1,3 mm and a size of 1,6 m^2 is prepared as described in example 2. After its finish it is still so air permeable that air can be blown through and has almost the same softness as prior to its finish.

Example 5:

For producing a leather with a nubuck type finish a backing of silicone rubber is used which, in addition to its rough surface, has fine depressions. The depressions for forming the nubuck type effect are introduced by laser treatment of the surface of the backing.

A particularly fine low viscous polyurethane dispersion with a solid material part of about 25 % is sprayed by means of a high pressure spraying nozzle onto the 40°C warm backing, which is joined to a support plate of aluminium sheet. The dispersion consists of more than 80 % by weight of non-thermoplastic polyurethane and contains 5 % cross-linking agent and 4 % of a 60 % acqeous silicone emulsion as well as pigments. The application quantity amounts to about 60 g/m^2. Thereafter the silicone backing is heated to 60°C and on it a polyurethane dispersion mixture, as described in example 1, is applied by means of two spray nozzles. These two dispersion applications form the finish with a fine net type texture.

A chromium tanned leather, of which its grain side is polished by means of buffing paper grain 320 and is milled for 8 hours, was cut into shaped sections for vehicle seats. Onto the shaped sections a bonding layer was applied as described in example 1. The pressing together also took place as mentioned in example 1. The completed leather has an attractive gripping pleasant nubuck surface and fulfils all parameters of the motor vehicle industry. It is water vapour permeable and it is possible to blow air through by the mouth.

It has been found that with the substrate in accordance with the invention not only the air and water vapour permeability but also the mechanical strength characteristics, in particular the wear and scratch resistance, are considerably improved, after completed cross-linking, particularly then if for the formation

of the finish known non-thermoplastic polyurethane dispersions and polyurethane dispersions, as known as adhesive starting materials, are applied. It has been found that an air throughflow of more than 10 l/minute at a pressure of 2 bar takes place with such a type of prepared substrate with an area of 100 cm^2.

By mixing such dispersions not only the required softening point can be varied but also other characteristics can be improved.

The substrate in accordance with the invention has, in comparison to known substrates, irrespective of the method used for producing it, at comparable thickness the finish of a considerably higher water permeability, and a high air permeability, which is absent with other substrates with comparable thickness of the finish. These substrates also fulfil the required CROCKMETERTEST in combination with MEK, stipulated by the US automobile industry. MEK passes into the pores of the substrate, but without damaging the surface and without causing colour variations.

Substrates, which are provided with a finish with nubuck surface, which has finest hairs, fulfil, in contrast to real nubuck leathers, all parameters stipulated by the motor vehicle industry. They can be maintained easily, do not become fatty, remain mat and, in contrast to synthetic nubuck, cannot burn and are temperature and solvent resistant.

Example 6:

The procedure is as follows in order to provide both a leather with a fine fibre suede type surface as well as a textile substrate, consisting of micro-fibres, with a fine fibre surface with a nubuck effect, so that both materials with the different substrates later on show the same surface, to be processed in combination in a vehicle or as upholstery cover.

The backing consists of silicone rubber and has in negative the nubuck texture, that means that the surface is rough and has depressions, which lead to the formation of the finest hairs or finest fibre tuffs. These depressions were applied into the backing tightly side-by-side by means of laser. This negative surface of the backing of silicone rubber was covered foil type by means of synthetic material in order to transfer the negative texture of the silicone surface positively onto the synthetic foil. This synthetic foil serves as master for forming silicone backings, in which in turn the nubuck texture is contained. This has the advantage that not each backing of silicone rubber has to be lasered, because in accordance with the invention the laser form can be multiplied by way of the master.

The backing has a thickness of 2 mm and is joined to an aluminium sheet by adhesive and has a length of 2 m and a width of 1,5 m. The backing is heated to a temperature of 66°C and under the conditions, as explained in example 1.

Simultaneously leather and a fleece material of micro-fibres, of which the hollow spaces are filled with a coagulating polyurethane, whereby it has a suede type surface formed by the projecting micro-fibres as described in example 1, are sprayed on by means of a synthetic dispersion, and after about 5 minutes both substrates are placed gripping dry onto the still warm backing and are pressed together under conditions, as given in example 1.

After about 15 seconds the material is removed from the press. It has the high quality nubuck effect with its fine projecting hairs, which shows a typical effect for nubuck.

Blowing through both nubuk materials is possible and after the cross-linking a cigarette can be pressed out on them, without damage. It also can be brought

into contact with many solvents, amongst others also with benzene and MEK, without damaging the surface.

Both materials have a clear pump effect, that means that during pressure, loading and relieving within a short time, an applied water drop passes through the finish into the substrate. Both materials with the nubuck type surface have, as compared to real nubuck leathers, the advantage that they do not become fatty. A relieved water drop, which is applied onto the surface, penetrates into the surface within two minutes without pump effect.

Prior to spraying the synthetic substrate material is always cut as shaped section or coarse shaped section out of a web.

A considerable advantage consists therein that the leather and the textile substrate are prepared of micro-fibres with the same nubuck surface and, if they are processed in combination, fit together optimally in colour and grip and age together, that is also after a long time period the finish of both materials has the same appearance.

The nubuck effect or grain effect in accordance with the invention is also of higher quality than the nubuck effect. Within the scope of the invention it is possible to provide coagulated and polished micro-fibre fleeces, such as for example Alcantara with its suede effect with a nubuck finish, which is optically of high quality and eliminate the disadvantages, such as lack in temperature consistency, soiling etc.